KOKAI PATENT APPLICATION NO. HEI 4-369

VAPOR-DEPOSITED FILM

[Translated from Japanesc]

[Translation No. LPX50788]

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JAPANESE PATENT OFFICE (JP)

KOKAI PATENT JOURNAL (A)

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Int. Cl.^{5}:	C 23 C 14/06 B 32 B 9/00 C 23 C 14/12 16/00
Identification Code:	A
Sequence Nos. for Office Use:	9046-4K 7639-4F 9046-4K 8722-4K
Application No.:	Hei 2-99933
Application Date:	April 16, 1990
Publication Date:	January 6, 1992 (Hei 4)
No. of Claims:	1 (Total of 4 pages in the [Japancse] document)
Examination Requested:	Not yet requested

Title of Invention:

VAPOR-DEPOSITED FILM

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[*There are no amendments to this patent.*]

Specification

1. Title of the invention

Vapor-deposited film

2. Claims of the invention

(1) A transparent vapor-deposited film characterized by the fact that a vapor-deposited film comprising a mixture of a polymer comprising a plasma polymerizable organic monomer and a metal oxide is formed on a polymer film substrate.

3. Detailed description of the invention

(Field of industrial application)

The present invention pertains to a vapor-deposited film in which a mixed film of a polymer and a metal oxide is formed on a polymer film, and the invention further pertains to a vapor-deposited film having superior adhesion between the polymer film and the aforementioned mixed film and having flexibility.

(Prior art)

Vapor-deposited films where vapor-deposited film of a metal or metal oxide is formed on a substrate such as polymer film by means of sputtering, ion plating, etc. are widely used in the field of medical product packaging, building interiors, and precision electronics as functional films.

In particular, films where a variety of vapor-deposited films are deposited on a substrate such as a polymer film have been used in the field of packaging, etc. in recent years.

However, for films produced by a standard vacuum deposition process, the adhesion between the polymer film and the aforementioned vapor-deposited film is insufficient or cracks are formed when external stress is applied at the time of deposition of the film and the initial function of the film is lost and the problems remain unsolved.

(Problems to be solved by the invention)

The purpose of the present invention is to produce a vapor-deposited metal oxide film with high adhesion to a polymer film.

(Means to solve the problem)

In order to achieve the aforementioned purpose, a transparent vapor-deposited film characterized by the fact that a vapor-deposited film comprising a mixture of a polymer made of a plasma-polymerizable organic monomer and a metal oxide is formed on a polymer film substrate is produced in the present invention.

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[Detailed description of the invention]

The polymer film substrate used in the present invention is a support for the aforementioned vapor-deposited film and polyolefins such as polyethylene, polypropylene, and polybutene; polystyrenes; polyesters such as polyethylene terephthalate, polybutylene terephthalate, and polyethylene-2,6-naphthalate, polyamides such as nylon 6 and nylon 12; polycarbonates; polyvinyl chlorides; polyvinylidene chlorides; aromatic polyamides, polyimides,

etc. may be used independently or in combination.

Furthermore, known additives, for example, antistatic agents, ultraviolet absorbers, plasticizers, lubricants, coloring matter, etc. may be included, as needed.

From the standpoint of strength, dimensional stability, and heat-resistance, an oriented polymer film substrate is desirable, but a non-oriented film may be used as well.

The thickness of the aforementioned polymer film substrate is not especially limited and from the standpoint of strength, etc. a thickness in the range of 3-400 μ is suitable, and 6-200 μ is further desirable.

For the shape of the polymer film substrate, a continuous strip is desirable, but three-dimensional trays, containers, bottles, etc. may be used as well.

For the plasma-polymerizable organic monomer used in the present invention, silicone type organic compounds can be used effectively. For example, siloxanes; tetraalkylsilanes such as tetramethylsilane, trimethylethylsilane and dimethyldiethylsilane; dialkylaminotrialkylsilanes such as diethylaminotrimethylsilane; hexaalkyldisilanes such as hexamethyldisilane and hexaethyldisilane, etc. can be mentioned, and from the standpoint of workability, hexamethyldisilane is further desirable.

For the metal oxide used in the present invention, magnesium oxide, aluminum oxide, tin oxide, titanium oxide, chromium oxide, silicon oxide, etc. can be mentioned and mixtures of same may be used as well.

The vapor-deposited film comprising a mixture of a plasma-polymerizable film and metal oxide used in the present invention is a thin film of amorphous plasma polymer made from a monomer gas of the aforementioned silicone type organic compound and the aforementioned metal oxide and it is not necessary for them to be mixed in a strict sense. For example, it may have a three layer structure comprising a plasma polymer film, metal oxide film, and plasma polymer film from the polymer film substrate side. Furthermore, a plasma polymer containing a metal oxide inside the film may be used as well.

The total thickness of the aforementioned vapor-deposited film is in the range of 500-5000 Å and in the range of 1000-2000 Å is further desirable.

In the case of the aforementioned three-layer structure, the plasma-polymerizable film may be very thin film and a thickness of 50-1000 Å provides a good effect.

In the vapor-deposited film of the present invention, the ratio of the Si comprising the amorphous plasma polymer made of the aforementioned silicone type organic metal compound and metal (M) comprising the aforementioned metal oxide film, M/Si, is in the range of 99.9-0.1 wt(%), and the optimum value varies depending on the type of metal oxide used.

Furthermore, a surface treatment such as a corona treatment, flame treatment, or discharge treatment may be provided for the polymer film substrate before forming the vapor-deposited film. And furthermore, a known resin primer agent may be applied as well.

The vapor-deposited film of the present invention may be formed by a method where known methods such as vacuum deposition and sputtering, PVD methods such as ion plating, and plasma CVD can be used in combination and any of the methods may be used. From the standpoint of quality of the film produced, reproducibility of the function and productivity, the DC method, RF method, ion plating based on the hollow cathode method are especially desirable.

Furthermore, a known protective layer, varnish layer, or printed layer may be formed on the aforementioned vapor-deposited film, or resins having heat-seal property such as polyethylene, polypropylene, and ethylene-vinyl acetate resin may be laminated by a conventional method to form a thickness in the range of 5-100 μ to provide a heat-seal property.

Fig. 1 shows an explanatory drawing of an example of a method for production of the vapor-deposited film of the present invention, and all of the interior of the device is maintained under a vacuum (A) of 10^{-5} to 10^{-6} Torr or below. The aforementioned silicon type organic compound is introduced to vacuum system (A) from induction port (5) through mass flow controller (MFC) (6) in such a manner that a vacuum of 10^{-2} to 10^{-4} Torr can be maintained; then, a plasma state is formed by high frequency coil (7) connected to high frequency power supply (71),

for example.

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(72) is a matching box. Under the aforementioned plasma state, standard vaporization source (4) is heated by heating unit (41) to vaporize the metal oxide (2) and it is continuously deposited onto continuously traveling polymer film substrate (1). In this case, the aforementioned polymer film substrate (1) travels from unwind roll (11) and passes through dancer roll (32), control roll (31), and expansion roll (33) and deposition takes place on chill roll (34). The aforementioned polymer film substrate (1) with the deposition film deposited on it is received on take-up roll (12) through expansion roll (33) and dancer roll (32).

(Working Example 1)

Using the machine shown in Fig. 2 [sic], a polyethylene terephthalate film with a thickness of 12 μ was mounted as the unwind roll, MgO was used as the deposition material, and the interior was exhausted by a vacuum unit to achieve $9x10^{-6}$ Torr.

Then, hexamethyldisilane was introduced as a gas and an adjustment was made to achieve $2x10^{-4}$ Torr with MFC and an oscillating field is provided by a high frequency (RF) power source at 13.56 MHz as matching is provided and stable discharge of plasma is provided.

Furthermore, vaporization of the MgO was initiated by electron beam heating and continuous film formation was provided onto the substrate film to form a film thickness of 1000 Å.

The vapor-deposited film produced was a clear, colorless film. When a film composition analysis of the aforementioned film was made, carbon, oxygen, magnesium and silicon were detected and the ratio of magnesium to silicon (Mg/Si) was 76.2:23.8 in terms of weight ratio. When an amorphous polypropylene (CPP) with a thickness of 60 μm was laminated onto the aforementioned film with a urethane type adhesive and the oxygen permeability was measured, a value of 1.2 cc/m^2/atm/day (MOCON OXTRAN 100 was used) was achieved and excellent results were obtained.

To evaluate adhesion of the vapor-deposited film, an attempt was made to measure the peel strength by peeling the resulting laminated film, but rupturing of the polyethylene terephthalate film occurred at 400 g/15 mm width and peeling was not possible.

Furthermore, when stress was applied to the aforementioned vapor-deposited film by a Garbo-flex [transliteration], and the gas barrier property and adhesion were evaluated, deterioration of the film caused by stress was absent and excellent properties were retained.

(Comparative Example 1)

In Working Example 1, hexamethyldisilane gas was omitted and MgO alone was deposited under the aforementioned conditions to produce a vapor-deposited film and when an evaluation was made of the gas barrier property, a value of approximately 1.3 cc/m^2/atm/day was achieved, but adhesion was insufficient and was 100 g/15 mm in terms of the laminated strength. Furthermore, when stress was applied as described above, the gas barrier property was reduced sharply to 5-30 cc/m^2/atm/day and a further reduction in adhesion was observed.

(Effect of the invention)

As explained in detail above, according to the polymer film of the present invention, the vapor-deposited film provided with a mixed film of a metal oxide and amorphous polymer on a polymer film substrate maintains the initial properties of the metal oxide film and still shows sufficient adhesion with the polymer film and furthermore, a film with sufficient flexibility for practical application can be produced.

4. Brief description of the figures

Fig. 1 shows an explanatory drawing of the apparatus used for production of the vapor-deposited film of the present invention.

Explanation of codes

1: polymer film

11: unwind roll

12: take-up roll

2: metal oxide

31: control roll

32: dancer roll

33: expansion roll

34: chill roll

4: deposition source

41: heat source

5: silicone type organic compound

6: MFC

7: high frequency coil

71: high frequency power supply

72: matching box

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Fig. 1